

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
20 February 2003 (20.02.2003)

PCT

(10) International Publication Number  
**WO 03/014014 A2**

(51) International Patent Classification<sup>7</sup>: **C01B 15/00**

(21) International Application Number: **PCT/EP02/08546**

(22) International Filing Date: **30 July 2002 (30.07.2002)**

(25) Filing Language: **English**

(26) Publication Language: **English**

(30) Priority Data:  
**MI2001A001688 2 August 2001 (02.08.2001) IT**

(71) Applicants (*for all designated States except US*): **ENI S.P.A. [IT/IT]; Piazzale E. Mattei, 1, I-00144 Roma (IT). POLIMERI EUROPA S.P.A. [IT/IT]; Via E. Fermi, 4, I-72100 Brindisi (IT).**

(72) Inventors; and

(75) Inventors/Applicants (*for US only*): **PAPARATTO, Giuseppe [IT/IT]; Via Vasari, 7, I-20092 Cinisello Balsamo (IT). DE ALBERTI, Giordano [IT/IT]; Largo Brianconi, 4, I-21010 Besnate (IT). D'ALOISIO, Rino [IT/IT]; Via Romentino, 25/E, I-28100 Novara (IT). BUZZONI, Roberto [IT/IT]; Via XXV Aprile, 72A, I-10099 San Mauro Torinese (IT).**

(74) Agents: **DE GREGORI, Antonella et al.; Ing. Barzanó & Zanardo Milano S.p.A., Via Borgonuovo, 10, I-20121 Milan (IT).**

(81) Designated States (*national*): **AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZM, ZW.**

(84) Designated States (*regional*): **ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).**

**Published:**

— *without international search report and to be republished upon receipt of that report*

*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

(54) Title: **CATALYST AND ITS USE IN THE SYNTHESIS OF HYDROGEN PEROXIDE**

(57) Abstract: The present invention relates to a catalyst consisting of: (a) one or more metals of the platinum group as active components; (b) one or more polyolefins; and (c) a carrier. The invention also relates to a process for the synthesis of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) from hydrogen and oxygen which uses said catalyst and the use of the hydrogen peroxide solution in oxidation processes catalyzed by titanium silicalite. The process operates under high safety conditions with a high productivity and molar selectivity towards the formation of H<sub>2</sub>O<sub>2</sub>.

5 CATALYST AND ITS USE IN THE SYNTHESIS OF HYDROGEN PEROXIDE

The present invention relates to a new catalyst, a process for the direct synthesis of hydrogen peroxide  
10 ( $H_2O_2$ ) from hydrogen and oxygen which uses said catalyst and the use of the hydrogen peroxide solution in oxidation processes catalyzed by titanium-silicalite.

Hydrogen peroxide is a commercially important compound which is widely applied as a bleach in the textile and pa-  
15 per industry, as a biocide in the environmental sector and in the chemical industry in oxidation processes.

Examples of these oxidation processes are those using titanium silicalite as catalysts, such as the epoxidation of olefins (EP 100,119), the ammoximation of carbonyl com-  
20 pounds (U.S. 4,794,198), the oxidation of ammonia to hydroxylamine (U.S. 5,320,819) and the hydroxylation of aromatic hydrocarbons (U.S. 4,369,783).

The industrial production of aqueous solutions of  $H_2O_2$  by means of a complex two-step process, is known.

25 In this process, a solution of anthraquinone, such as

butylanthraquinone or ethylanthraquinone, in an organic medium immiscible with water, is first hydrogenated and then oxidized with air to produce  $H_2O_2$  which is subsequently extracted in aqueous phase.

5        This process, however, has substantial disadvantages deriving from the necessity of operating with large volumes of reagents, the numerous steps required, the relatively high cost of the intermediates and the formation of by-products.

10        In order to overcome these drawbacks, processes have been studied for the direct synthesis of hydrogen peroxide from  $H_2$  and  $O_2$ . These processes are generally carried out by reacting the two gases in a solvent consisting of an aqueous medium or an aqueous-organic medium, in the presence of a suitable catalytic system.

15        Among processes of this type, those which operate in an alcohol or alcohol-aqueous medium, for example in methanol or in methanol-water described, for example, in U.S. patent 4,335,092, in patent application WO 98/16463, in  
20        European patent application EP 787681 and more particularly in European patent application EP 978316 and in Italian patent applications MI 2000 A001218, MI 2000 A001219 and MI 2000 A001881, appear attractive from a technical and economic point of view.

25        With the same conditions in fact, higher reaction

rates and selectivities have been observed with respect to when operating in an aqueous medium.

The high reaction performances lead in turn to:

- i) the possibility of carrying out the process under high safety conditions, well outside the explosivity zone of  $H_2-O_2$  mixtures, without jeopardizing it from a technical-economic point of view;
- ii) the possibility of using extremely low quantities of promoters (halides and acids) in the reaction medium, with beneficial effects on the stability of the catalytic system and formation of hydrogen peroxide solutions which are stable and at an adequate concentration for direct and economically valid use in oxidation processes.

Finally, the concentration of the solutions of hydrogen peroxide produced is facilitated up to commercially useful values, as the boiling point and evaporation heat of the suitably selected alcohol are lower than those of water.

These processes are generally carried out in the presence of a catalytic system consisting of a noble metal, particularly metals of the platinum group or their mixtures, in the form of salts or as supported metals.

It has now been found that it is possible to further improve these processes, in terms of selectivity and cost,

using a heterogeneous catalyst consisting of one or more metals of the platinum group, one or more polyolefins and a carrier.

The use of polyolefins also allows the mechanical properties of the catalyst to be improved and facilitates its filtration from the reaction mixture.

An objective of the present invention therefore relates to a heterogeneous catalyst consisting of one or more metals of the platinum group, one or more polyolefins and a carrier.

Another objective of the present invention relates to a process for the production of hydrogen peroxide starting from hydrogen and oxygen, which uses said catalyst.

A further objective of the present invention relates to the use of solutions of hydrogen peroxide obtained as described above in an oxidation process catalyzed by titanium silicalite.

The catalyst which can be used for the purposes of the invention is a heterogeneous catalyst consisting of:

- (a) one or more metals of the platinum group as active components;
- (b) one or more polyolefins; and
- (c) a carrier.

Examples of metals of the platinum group are: palladium, platinum, ruthenium, rhodium and iridium. Preferred

metals are palladium and platinum.

In these catalysts, the palladium is normally present in a quantity ranging from 0.01 to 4% by weight and the platinum in a quantity ranging from 0.001 to 1% by weight, with an atomic ratio between platinum and palladium ranging from 0.1/99.9 to 50/50.

The palladium is preferably present in a quantity ranging from 0.05 to 2% by weight and the platinum in a quantity ranging from 0.005 to 0.5% by weight, with an atomic ratio between platinum and palladium ranging from 1/99 to 30/70.

In addition to palladium and platinum, other metals such as ruthenium, rhodium, iridium and gold can be present as active components or promoters, in a concentration generally not higher than that of the palladium.

The polyolefins which can be used in the process of the present invention have a molecular weight higher than 400 and are selected from:

- homopolymers of ethylene and copolymers of ethylene with alpha olefins;
- homopolymers of propylene and copolymers of propylene with alpha olefins;
- homopolymers of butadiene and copolymers with styrene and other olefins;
- homopolymers of isoprene and copolymers with other ole-

fins;

- ethylene/propylene (EPR) copolymers;
- ethylene/propylene/diolefin (EPDM) terpolymers;
- thermoplastic elastomers deriving from butadiene and/or
- 5 isoprene and styrene block copolymers, hydrogenated and non-hydrogenated.

The preferred polyolefins are amorphous polyolefins as they are more soluble and therefore easier to disperse on the carrier.

10 For the purposes of the present invention rubbers are particularly preferred, and, in general, commercial copolymers of butadiene-styrene (synthetic rubber; GRS, SBR); ethylene-propylene (EPM, EPR) copolymers, ethylene-propylene-diene copolymers (EPDM rubbers), styrene-  
15 butadiene-styrene (SBR thermoplastic rubbers); isobutylene-isoprene (butyl rubbers).

The polyolefins which can be used for the purposes of the present invention can be prepared according to any of the methods known in the art.

20 The quantity of polyolefin used ranges from 0.1 to 20% by weight, preferably from 1 to 10% by weight, with respect to the catalyst.

The inert carrier may typically consist of activated carbon, silica, alumina, silica-alumina, zeolites, and  
25 other materials well known in the state of the art. Acti-

vated carbon is preferably used for the preparation of the catalysts useful for the invention.

Activated carbons which can be used for the purposes of the invention are selected from those of a fossil or natural origin deriving for example from wood, lignite, 5 peat or coconut and having a surface area higher than 100 m<sup>2</sup>/g, preferably higher than 300 m<sup>2</sup>/g and a carbon with a surface area higher than 600 m<sup>2</sup>/g is particularly preferred. Preferred activated carbons are those with a low 10 ash content.

The sulfonated activated carbons described in European patent application EP 978316 can be used for the purpose.

Before the deposition of the metals or polyolefins, the activated carbon can be subjected to treatment such as 15 washing with distilled water or treatment with acids, bases or diluted oxidizing agents, for example acetic acid, hydrochloric acid, sodium carbonate and hydrogen peroxide.

The catalyst can be prepared by dispersing the active components on the inert carrier or pretreated with the 20 polyolefin, by means of precipitation and/or impregnation starting from precursors consisting for example of solutions of their salts or soluble complexes, and then reduced to the metallic state by means of thermal and/or chemical treatment with reducing substances such as hydrogen, sodium 25 formiate, sodium citrate or by preparative techniques well



known in the art.

According to an embodiment of the present invention, the catalyst can be prepared by dispersing in sequence and alternating the precursors of the single metal components of the catalyst onto the carrier, as described and claimed in patent application IT MI2000-A001219.

The polyolefin is generally dissolved in a suitable solvent and the resulting solution is used to impregnate the carrier.

10 The dry impregnation technique is preferably used, which consists in putting the polyolefin mixture in contact with the carrier, in a closed reactor at 100-120°C, for 2-3 hours, in order to facilitate the depositing of the polymer onto the surface. At the end, the solvent is evaporated at  
15 a temperature of 140°C for 3-4 hours.

Examples of solvents suitable for the purposes of the present invention are selected from paraffins, aromatic hydrocarbons and cyclo-paraffins. N-heptane, toluene, decaline, n-decane are preferably used.

20 In the preparation of the catalyst, the sequence with which the metals of the platinum group (a) and polyolefins (b) are put in contact with the carrier, is not particularly critical.

When a quantity of polyolefins higher than 5% by  
25 weight is used, however, it is preferable to disperse the

mixture of polyolefins onto the carrier after depositing the metals forming the active phase.

The catalyst of the present invention is particularly advantageous in a process for the preparation of hydrogen peroxide from hydrogen and oxygen in a reaction solvent containing a halogenated promoter and/or an acid promoter.

The catalyst is normally dispersed in the reaction medium at a concentration ranging from 0.1 to 10% by weight, preferably from 0.3 to 3% by weight with respect to the reaction solvent.

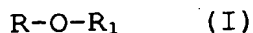
The reaction solvent consists of one or more alcohols or an alcohol-water mixture to which an aliphatic ether and/or one or more C<sub>5</sub>-C<sub>32</sub> hydrocarbons are optionally added.

Examples of alcohols suitable for the purposes of the present invention are selected from those with from 1 to 6, preferably from 1 to 4, carbon atoms.

Among C<sub>1</sub>-C<sub>4</sub> alcohols, methanol, ethanol, terbutanol (TBA) or their mixtures, are preferred. Methanol is particularly preferred. Among the preferred mixture is a mixture of methanol and water.

The quantity of alcohol(s) ranges from 30 to 99% by weight with respect to the mixtures, preferably from 50 to 98% by weight.

The aliphatic ethers are selected from those having general formula (I)



wherein R and R<sub>1</sub>, the same or different, are alkyl groups with from 1 to 6 carbon atoms. In the compounds having formula (I), R is preferably methyl and R<sub>1</sub> a ter-alkyl.

5 Methyl-terbutylether (MTBE) is particularly preferred.

The quantity of ethers which is used in the solvent mixture depends on the type of alcohol(s) used and generally ranges from 0 to 70% by weight, preferably from 10 to 60% by weight, with respect to the reaction solvent.

10 According to an embodiment of the process of the present invention, the reaction solvent can also contain one or more C<sub>5</sub>-C<sub>32</sub> hydrocarbons.

These hydrocarbons are generally selected from paraffins, cyclo-paraffins or aromatic compounds.

15 Examples of paraffinic hydrocarbons are preferably selected from those having from 5 to 18 carbon atoms, and can be linear or branched.

Examples of said paraffinic hydrocarbons are n-hexane, n-heptane, n-octane, n-decane or their branched isomers.

20 Examples of cyclo-paraffinic hydrocarbons are cyclohexane, decaline or their derivatives substituted with one or more alkyl groups with from 1 to 6 carbon atoms. Typical examples of these compounds are methyl-cyclohexane, ethyl-cyclohexane or dimethyl-cyclohexane.

25 Aromatic hydrocarbons suitable for the purposes of the

present invention are preferably selected from those having from 6 to 24 carbon atoms.

Examples of aromatic hydrocarbons are benzene, naphthalene, alkylbenzenes and alkylnaphthalenes with one or  
5 more alkyl chains, linear or branched, having from 1 to 18, preferably from 6 to 12 carbon atoms.

Examples of alkylbenzenes are toluene, xylenes (ortho, meta and para), ethylbenzene and cumene.

The quantity of hydrocarbons which is used in the re-  
10 action depends on the type of alcohol(s) used and generally ranges from 0 to 20% by weight, preferably from 0.1 to 10% by weight, with respect to the reaction solvent.

The acid promoter may be any substance capable of generating  $H^+$  hydrogen ions in the reaction solvent and is  
15 generally selected from inorganic acids such as sulfuric, phosphoric, nitric acid or from organic acids such as sulfonic acids. Sulfuric acid and phosphoric acid are preferred.

The concentration of the acid generally ranges from 20  
20 to 1000 mg per kg of reaction solvent and preferably from 50 to 500 mg per kg of reaction solvent.

The halogenated promoter can be any substance capable of generating halide ions in the reaction solvent. Substances capable of generating bromide ions are preferred.  
25 These substances are generally selected from hydrobromic

acid and its salts soluble in the reaction medium, for example sodium bromide, potassium bromide, ammonium bromide or sodium bromate. Hydrobromic acid, sodium bromide and potassium bromide are particularly preferred.

5       The concentration of the halogenated promoter generally ranges from 0.1 to 50 mg per kg of reaction solvent and preferably from 1 to 10 mg per kg of reaction solvent.

      The production of hydrogen peroxide is carried out by reacting oxygen and hydrogen in the reaction solvent in the  
10   presence of the catalyst and promoters and in the presence or absence of an inert gas selected from nitrogen, helium, argon. Nitrogen is the preferred gas.

      The molar ratio  $H_2/O_2$  in the feeding ranges from 1/1 to 1/100, preferably from 1/2 to 1/15 and the concentration  
15   of hydrogen in the gaseous phase in contact with the reaction solvent is conveniently maintained at a value lower than 4.5% molar, outside the explosivity limits of the mixture consisting of  $H_2$ ,  $O_2$  and, optionally, an inert gas.

      According to an embodiment of the process of the present  
20   invention, the reaction can be carried out using air instead of pure oxygen.

      The reaction is typically carried out at temperatures ranging from  $-5^\circ$  to  $90^\circ C$ , preferably from 2 to  $50^\circ C$ , a temperature ranging from 20 to  $40^\circ C$  is particularly preferred,  
25   and at a total pressure higher than atmospheric pressure,

preferably ranging from 10 to 300 bars, 30-100 bars being particularly preferred.

The process according to the present invention can be carried out batchwise or, preferably, in continuous using a reactor suitable for the purpose and selected from those  
5 described in the state of the art.

Operating under the above conditions, it is possible to produce hydrogen peroxide under safety conditions with a reaction productivity normally ranging from 30 to 200 g of  
10  $H_2O_2$  (expressed as  $H_2O_2$  at 100%) per litre of reaction medium per hour and with a molar selectivity towards the formation of  $H_2O_2$ , referring to the hydrogen used up, ranging from 60% to 90%.

The solutions of hydrogen peroxide thus obtained can  
15 be used directly in oxidation processes which comprise the use of  $H_2O_2$  without onerous intermediate processing such as the removal of acids and solvents.

Furthermore, the process of the present invention is suitable for the production of aqueous solutions of  $H_2O_2$   
20 having a commercial titer, by the removal of the organic components from the reaction medium, for example by distillation, which can be recycled to the synthesis.

The process of the present invention allows the reagents to be transformed into  $H_2O_2$  with high conversions and  
25 selectivities, obtaining  $H_2O_2$  solutions without acidity or

containing only traces of acidity and/or salts.

The following examples, which have the sole purpose of describing the present invention in greater detail, should in no way be considered as limiting its scope.

5 EXAMPLE 1

Treatment of the activated carbon carrier

150 g of activated carbon of maritime pine charcoal in powder form (CECA/2S/E) and 1500 ml of distilled water are charged into a 2 liter jacketed glass flask, thermostat-  
10 regulated with an oil-heated bath and equipped with a cooler and stirring. After 2 hours at 80°C, the activated carbon is filtered and washed with distilled water.

The activated carbon, still damp, is then charged into the 2 liter glass flask described above and after adding  
15 1500 ml of a solution at 5% by weight of HCl, the temperature is brought to 80°C. After about 2 hours, the mixture is cooled and the activated carbon is washed on a filter with distilled H<sub>2</sub>O until the chlorides have been eliminated. The washed activated carbon is recovered and dried  
20 in an oven at 120°C for 3 hours.

EXAMPLE 2 (comparative)

Preparation of the catalyst Pt-Pd/C (EX2)

(a) 900 ml of distilled water, 2.8 g of Na<sub>2</sub>CO<sub>3</sub> and subsequently 80 g of activated carbon prepared in Example  
25 1, are charged into a glass reactor, having the character-

istics described in Example 1. The suspension is maintained at room temperature (20-25°C), under stirring, for 10 minutes.

A solution of 8 g of  $\text{Na}_2\text{PdCl}_4$  at 10% by weight of Pd in 100 ml of distilled water are subsequently added dropwise over a period of about 10 minutes and the resulting suspension is kept at room temperature for 10 minutes and is then heated in a water bath for 10 minutes to 90°C. A solution containing 0.76 g of sodium formate in 100 ml of distilled water is then added and the stirring is continued at 90°C for 2 hours.

After cooling to room temperature, the suspension is filtered and the recovered catalyst is washed with distilled water until the chlorides have been eliminated and dried in an oven at 120°C for 3 hours.

(b) the catalyst thus obtained is put in the 2 litre reactor described above and treated following the procedure described in (a), but using a solution of 0.404 g of  $\text{H}_2\text{PtCl}_6$  (8% by weight of Pt) instead of the solution of  $\text{Na}_2\text{PdCl}_4$ .

After drying at 120°C, a catalyst is obtained (EX2) containing 0.97% of Pd and 0.038% of Pt on activated carbon.

### EXAMPLE 3

Preparation of activated Carbons functionalized with sul-



fonic groups (C-SO<sub>3</sub>H)

80 g of activated carbon prepared as described in Example 1 are charged into a jacketed 2 litre glass reactor, thermostat-regulated with an oil-heated bath and equipped with a cooler and stirring, and 240 g of H<sub>2</sub>SO<sub>4</sub> at 96% are added dropwise in 20 minutes. After homogenizing the mixture with slight stirring, it is heated to 140°C for 2 hours.

The mixture is cooled to room temperature and 200 g of crushed ice (from distilled water) are added in 10 minutes, the mixture is left to cool, a further 1000 ml of distilled water are added, the contents of the reactor are recovered and filtered. The activated carbon thus treated is washed until the sulfate ion in solution has been eliminated.

Upon elemental analysis, the activated carbon thus treated contains 0.38% of S.

EXAMPLE 4 (comparative)Preparation of the catalyst Pd-Pt/C-SO<sub>3</sub>H (EX4)

The same procedure is adopted as described in Example 2, but using as carrier 8 g of activated carbon functionalized as specified in Example 3. The catalyst (EX4) is obtained, which upon analysis contains: 0.039% Pt; 0.98% Pd; 0.35% S.

EXAMPLE 5

Preparation of the catalyst Pt-Pd/C+2.9%polySTY

8 g of the catalyst EX2 are charged into a 200 ml glass vacuum flask and flushed with nitrogen for 15 minutes to eliminate the air.

0.24 g of polystyrene (average MW 120000) are dissolved at 70°C in a 100 ml Erlenmeyer flask containing 24 g of toluene. The resulting solution is then added dropwise in 5 minutes, maintaining the stream of nitrogen, into the flask containing the catalyst EX2. The flask containing the catalyst to which the polymer has been added is put under a rotating evaporator and is slowly reflux heated to 110°C for 3 hours. The toluene is distilled under a slight vacuum, the catalyst is poured into a 100 ml glass and dried in an oven at 140°C for 3 hours.

The catalyst (EX5) is obtained, containing upon analysis: (Pt-Pd/C)+2.9%polySTY (0.036% Pt; 0.94% Pd).

#### EXAMPLE 6

##### Preparation of the catalyst Pt-Pd/C-SO<sub>3</sub>H+3%polySTY (EX6)

The same procedure is adopted as described in Example 5, but using the catalyst EX4 prepared in Example 4.

The catalyst (EX6) is obtained containing upon analysis: Pt-Pd/C-SO<sub>3</sub>H+3%polySTY (0.035% Pt; 0.93% Pd and 0.36% S).

#### EXAMPLE 7

##### Preparation of the catalyst Pt-Pd/C (C<sub>2</sub>-co-C<sub>3</sub>) (EX8)

The same procedure is adopted as described in Example

5, but using 0.24 g of 65% ethylene-35% propylene copolymer (EPR rubber) with an average molecular weight of 110000 instead of the polystyrene. The catalyst is obtained (EX8) containing upon analysis: Pt-Pd/(C+2.9%C<sub>2</sub>-co-C<sub>3</sub>) (0.036% Pt; 0.94% Pd).

#### EXAMPLE 8

##### Preparation of the catalyst Pt-Pd/C-SO<sub>3</sub>H(C<sub>2</sub>-co-C<sub>3</sub>) (EX10)

The same procedure is adopted as described in Example 7, but using 8 g of the catalyst EX4 of Example 4.

10 The catalyst is obtained (EX10) containing upon analysis: Pt-Pd/(C-SO<sub>3</sub>H+2.9%C<sub>2</sub>-co-C<sub>3</sub>) (0.036% Pt; 0.95% Pd; 0.37% S).

#### EXAMPLES 9-10

Examples 5 and 6 are repeated using 0.24 g of butadiene-styrene copolymer (SBR: 75/25) with an average molecular weight of 120000 instead of the C<sub>2</sub>-C<sub>3</sub> copolymer.

The catalysts (EX12 and EX14) are obtained respectively, containing upon analysis:

EX 12: Pt-Pd/(C +2.9%SBR) (0.036% Pt; 0.95% Pd).

EX 14: Pt-Pd/(C-SO<sub>3</sub>H+2.9%SBR) (0.036% Pt; 0.94% Pd; 0.36% S).

#### EXAMPLES 11-18

##### Synthesis of hydrogen peroxide

A micropilot plant is used, consisting of a Hastelloy C autoclave having a volume of 400 ml, equipped with a thermostat-regulation system, a magnetic drag stirring sys-

tem, a regulation and control system of the pressure during the reaction, a filter for continuously removing the liquid phase containing the reaction products, a feeding system of the mixture of solvent and promoters in which the reaction takes place, a feeding system of the gaseous reagents and a series of regulation and control instruments.

The reaction trend is followed by continuously analyzing the hydrogen and oxygen in the feeding and at the outlet of the reactor.

10       The concentration of  $H_2O_2$  which is formed is determined in the liquid effluent of the reactor by titration with potassium permanganate. The selectivity with respect to the converted hydrogen is calculated on the basis of the concentration of  $H_2O_2$  in the reaction effluent and on the basis of the analysis of the  $H_2$  leaving the reactor, once the stationary state has been reached.

15       1.0 g of catalyst prepared as described in examples 2, 4 and 5-8 and 100 g of methanol:water solution (97/3 by weight) containing 6 ppm of HBr (6 mg/kg) and 200 ppm of  $H_2SO_4$  (200 mg/kg) are charged into the reactor.

20       The autoclave is pressurized, without stirring, at 60 bars with a gaseous mixture consisting of 3.6% of  $H_2$ , 11% of  $O_2$  and 85.4% of  $N_2$ . The stirring is then started up to 800 revs/minute, the pressure is maintained with a continuous stream, 916 normal liters (Nl), of the same gaseous

mixture, with the contemporaneous feeding of 400 g/hour of a methanol:water solution having the composition defined above and containing 6 ppm of HBr and 200 ppm of H<sub>2</sub>SO<sub>4</sub>.

The temperature inside the reactor is maintained at 25°C.

- 5        The results obtained after 50 hours of reaction are indicated in Table 1.

Table 1

Catalyst	H <sub>2</sub> O <sub>2</sub> %	Selectivity %
EX2 Pt-Pd/C	5.3	64
EX4 Pt-Pd/C-SO <sub>3</sub> H	5.7	70
EX5 Pt-Pd/C + 3% polysty	5.6	73
EX6 Pt-Pd/C-SO <sub>3</sub> H + 3% polysty	5.9	80
EX8 Pt-Pd/(C+(C <sub>2</sub> -co-C <sub>3</sub> ))	5.6	71
EX10 Pt-Pd/(C-SO <sub>3</sub> H+(C <sub>2</sub> -co-C <sub>3</sub> ))	6.0	78
EX12 Pt-Pd/(C+SBR(25-75))	5.8	74
EX14 Pt-Pd/((C-SO <sub>3</sub> H(SBR(25-75)))	5.8	81

CLAIMS

1. A catalyst useful for the synthesis of hydrogen peroxide starting from hydrogen and oxygen consisting of:
  - (a) one or more metals of the platinum group as active components;
  - (b) one or more polyolefins; and
  - (c) a carrier:
2. The catalyst according to claim 1, wherein the metal components of the catalyst are selected from palladium, platinum, ruthenium, rhodium and iridium.
3. The catalyst according to claim 2, wherein the metal components of the catalyst are palladium and platinum.
4. The catalyst according to claim 3, wherein the quantity of palladium ranges from 0.01 to 4% by weight and the quantity of platinum ranges from 0.001 to 1% by weight, with an atomic ratio platinum/palladium ranging from 0.1/99.9 to 50/50.
5. The catalyst according to claim 4, wherein the quantity of palladium ranges from 0.05 to 2% by weight and the quantity of platinum ranges from 0.005 to 0.5% by weight, with an atomic ratio platinum/palladium ranging from 1/99 to 30/70.
6. The catalyst according to claim 3, wherein in addition to palladium and platinum other metals such as, for example, ruthenium, rhodium, iridium and gold can also

be present as active components or promoters, in a concentration not higher than that of the palladium.

7. The catalyst according to claim 1, wherein the polyolefins have a molecular weight higher than 400 and are selected from:

- homopolymers of ethylene and copolymers of ethylene with alpha olefins;
  - homopolymers of propylene and copolymers of propylene with alpha olefins;
  - homopolymers of butadiene and copolymers with styrene and other olefins;
  - homopolymers of isoprene and copolymers with other olefins;
  - ethylene/propylene (EPR) copolymers;
  - ethylene/propylene/diolefin (EPDM) terpolymers;
  - thermoplastic elastomers deriving from butadiene and/or isoprene and styrene block copolymers, hydrogenated and non-hydrogenated.
8. The catalyst according to claim 7, wherein the polyolefins are amorphous polyolefins.
9. The catalyst according to claim 7, wherein the polyolefins are selected from rubbers and copolymers of butadiene-styrene (synthetic rubber; GRS, SBR); ethylene-propylene (EPM, EPR) copolymers, ethylene-propylene-diene copolymers (EPDM rubbers), styrene-

butadiene-styrene (SBR thermoplastic rubbers); isobutylene-isoprene (butyl rubbers).

10. The catalyst according to claim 1, wherein the quantity of polyolefin ranges from 0.1 to 20% by weight with respect to the catalyst.
11. The catalyst according to claim 10, wherein the quantity of polyolefin ranges from 1 to 10% by weight with respect to the catalyst.
12. The catalyst according to claim 1, wherein the carrier is selected from activated carbon, activated carbon functionalized with sulfonic groups, silica, alumina, silica-alumina and zeolites.
13. The catalyst according to claim 12, wherein the carrier is an activated carbon with a low ash content and a surface area higher than  $100 \text{ m}^2/\text{g}$ .
14. The catalyst according to claim 13, wherein the activated carbon has a surface area higher than  $300 \text{ m}^2/\text{g}$ .
15. The catalyst according to claim 14, wherein the activated carbon has a surface area higher than  $600 \text{ m}^2/\text{g}$ .
16. The catalyst according to claim 1, prepared by dispersing the active components on an inert carrier or pretreated with polyolefins by means of precipitation and/or impregnation.
17. The catalyst according to claim 16, prepared by dispersing in sequence and alternating the precursors of

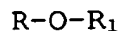


the single metal components of the catalyst on an inert carrier or pretreated with polyolefins.

18. A process for the production of hydrogen peroxide from hydrogen and oxygen in a reaction solvent containing a halogenated promoter and/or an acid promoter, in the presence of a catalyst according to claims 1 to 17.
19. The process according to claim 18, wherein the reaction solvent consists of one or more alcohols or a mixture of alcohol-water optionally containing an aliphatic ether and/or one or more C<sub>5</sub>-C<sub>32</sub> hydrocarbons.
20. The process according to claim 19, wherein the alcohol is selected from those having from 1 to 6 carbon atoms.
21. The process according to claim 20, wherein the alcohol is selected from those having from 1 to 4 carbon atoms.
22. The process according to claim 21, wherein the alcohol is selected from methanol, ethanol, terbutanol (TBA) or their mixtures.
23. The process according to claim 22, wherein the alcohol is methanol.
24. The process according to claim 19, wherein the quantity of alcohol(s) ranges from 30 to 99% by weight with respect to the mixture.
25. The process according to claim 24, wherein the quan-

tity of alcohol(s) ranges from 50 to 98% by weight with respect to the mixture.

26. The process according to claim 19, wherein the aliphatic ether is selected from those defined by general formula (I)



wherein R and R<sub>1</sub>, the same or different, are alkyl groups having from 1 to 6 carbon atoms.

27. The process according to claim 26, wherein in the compounds having formula (I), R is methyl and R<sub>1</sub> a tertiary alkyl.

28. The process according to claim 27, wherein the ether is methyl-terbutylether (MTBE).

29. The process according to claim 19, wherein the quantity of aliphatic ether having general formula (I) ranges from 0 to 70% by weight with respect to the reaction solvent.

30. The process according to claim 29, wherein the quantity of aliphatic ether having general formula (I) ranges from 10 to 60% by weight with respect to the reaction solvent.

31. The process according to claim 19, wherein the C<sub>5</sub>-C<sub>32</sub> hydrocarbons are selected from paraffins, cycloparaffins and aromatic compounds.

32. The process according to claim 31, wherein the para-

finic hydrocarbons can be linear or branched.

33. The process according to claim 32, wherein the paraffinic hydrocarbons are selected from those having from 5 to 18 carbon atoms.
- 5 34. The process according to claim 33, wherein the paraffinic hydrocarbons are selected from n-hexane, n-heptane, n-octane, n-decane or their branched isomers.
35. The process according to claim 31, wherein the cycloparaffinic hydrocarbons are selected from cyclohexane, decaline or their derivatives substituted with one or  
10 more alkyl groups having from 1 to 6 carbon atoms.
36. The process according to claim 35, wherein the substituted cyclo-paraffins are selected from methylcyclohexane, ethyl-cyclohexane and dimethyl-cyclohexane.  
15
37. The process according to claim 31, wherein the aromatic hydrocarbons are selected from those having from 6 to 24 carbon atoms.
38. The process according to claim 37, wherein the aromatic hydrocarbons are selected from benzene, naphthalene, alkylbenzenes and alkylnaphthalenes with one or  
20 more linear or branched alkyl chains having from 1 to 18 carbon atoms.
39. The process according to claim 38, wherein the alkylbenzenes and alkylnaphthalenes have a linear or  
25

branched alkyl chain having from 6 to 12 carbon atoms.

40. The process according to claim 39, wherein the alkylbenzenes are selected from toluene, xylenes (ortho, meta and para), ethylbenzene and cumene.
- 5 41. The process according to claim 19, wherein the quantity of hydrocarbons ranges from 0 to 20% by weight with respect to the reaction solvent.
42. The process according to claim 41, wherein the quantity of hydrocarbons ranges from 0.1 to 10% by weight  
10 with respect to the reaction solvent.
43. The process according to claim 18, wherein the catalyst is used at a concentration ranging from 0.1 to 10% by weight with respect to the reaction solvent.
44. The process according to claim 43, wherein the cata-  
15 lyst is used at a concentration ranging from 0.3 to 3% by weight with respect to the reaction solvent.
45. The process according to claim 18, wherein the acid promoter is selected from substances capable of generating  $H^+$  hydrogen ions in the reaction solvent.
- 20 46. The process according to claim 45, wherein the acid promoter is selected from inorganic acids such as sulfuric, phosphoric, nitric acid or from organic acids such as sulfonic acids.
47. The process according to claim 46, wherein the acid  
25 promoter is sulfuric acid or phosphoric acid.

48. The process according to claim 18, wherein the concentration of acid promoter ranges from 20 to 1000 mg per kg of reaction solvent.
49. The process according to claim 48, wherein the concentration of acid promoter ranges from 50 to 500 mg per kg of reaction solvent.
50. The process according to claim 18, wherein the halogenated promoter is selected from substances capable of generating halogen ions in the reaction solvent.
51. The process according to claim 50, wherein the halogenated promoter is selected from substances capable of generating bromide ions such as hydrobromic acid and its salts soluble in the reaction medium such as alkaline bromides, ammonium bromide or sodium bromate.
52. The process according to claim 51, wherein the compound is hydrobromic acid, sodium bromide or potassium bromide.
53. The process according to claim 18, wherein the concentration of halogenated promoter ranges from 0.1 to 50 mg per kg of reaction solvent.
54. The process according to claim 53, wherein the concentration of halogenated promoter ranges from 1 to 10 mg per kg of reaction solvent.
55. The process according to claim 18, wherein the reaction is carried out at a temperature ranging from -5

to 90°C.

56. The process according to claim 55, wherein the temperature ranges from 2 to 50°C.
57. The process according to claim 56, wherein the temperature ranges from 20 to 40°C.
58. The process according to claim 18, wherein the reaction is carried out at a total pressure higher than atmospheric pressure.
59. The process according to claim 58, wherein the total pressure ranges from 10 to 300 bars.
60. The process according to claim 59, wherein the total pressure ranges from 30 to 100 bars.
61. The process according to claim 18, wherein the molar ratio hydrogen/oxygen in the feeding ranges from 1/1 to 1/100.
62. The process according to claim 61, wherein the molar ratio hydrogen/oxygen in the feeding ranges from 1/2 to 1/15.
63. The process according to claim 18, wherein the reaction is carried out in the presence of an inert gas selected from nitrogen, helium, argon.
64. The process according to claim 63, wherein the inert gas is nitrogen.
65. The process according to claim 18, wherein the concentration of hydrogen in the gaseous phase in contact

with the reaction solvent is maintained at a value lower than 4.5% molar.

66. The process according to claim 18, wherein the reaction is carried out using air as oxygen source.

5 67. The process according to claim 18, wherein the reaction is carried out batchwise or in continuous.

68. The process according to claim 18, wherein the solution of hydrogen peroxide is used directly in an oxidation process of a substrate selected from olefins, aromatic hydrocarbons, ammonia and carbonyl compounds, using titanium silicalite as catalyst.

10

69. The process according to claim 18, wherein the solution of hydrogen peroxide is used to obtain aqueous solutions having a commercial titer of  $H_2O_2$  by the removal, from the reaction medium, of the organic components which can be recycled to the synthesis.

15

**THIS PAGE BLANK (USPTO)**



(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
20 February 2003 (20.02.2003)

PCT

(10) International Publication Number  
**WO 03/014014 A3**

(51) International Patent Classification<sup>7</sup>: **C01B 15/029**,  
21/26, B01J 23/42, 23/44, 31/06, C07D 301/12, C07C  
249/04, C07D 303/04

(74) Agents: **DE GREGORI**, Antonella et al.; Ing. Barzanó  
& Zanardo Milano S.p.A., Via Borgonuovo, 10, I-20121  
Milan (IT).

(21) International Application Number: PCT/EP02/08546

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU,  
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU,  
CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH,  
GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC,  
LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW,  
MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG,  
SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ,  
VN, YU, ZA, ZM, ZW.

(22) International Filing Date: 30 July 2002 (30.07.2002)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
MI2001A001688 2 August 2001 (02.08.2001) IT

(84) Designated States (*regional*): ARIPO patent (GH, GM,  
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW),  
Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),  
European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE,  
ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SK,  
TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ,  
GW, ML, MR, NE, SN, TD, TG).

(71) Applicants (*for all designated States except US*): **ENI**  
S.P.A. [IT/IT]; Piazzale E. Mattei, 1, I-00144 Roma (IT).  
**POLIMERI EUROPA S.P.A.** [IT/IT]; Via E. Fermi, 4,  
I-72100 Brindisi (IT).

(72) Inventors; and

(75) Inventors/Applicants (*for US only*): **PAPARATTO**,  
Giuseppe [IT/IT]; Via Vasari, 7, I-20092 Cinisello Bal-  
samo (IT). **DE ALBERTI**, Giordano [IT/IT]; Largo  
Brianzoni, 4, I-21010 Besenzone (IT). **D'ALOISIO**, Rino  
[IT/IT]; Via Romentino, 25/E, I-28100 Novara (IT). **BUZ-**  
**ZONI**, Roberto [IT/IT]; Via XXV Aprile, 72A, I-10099  
San Mauro Torinese (IT).

Published:

— with international search report

(88) Date of publication of the international search report:  
17 July 2003

For two-letter codes and other abbreviations, refer to the "Guid-  
ance Notes on Codes and Abbreviations" appearing at the begin-  
ning of each regular issue of the PCT Gazette.

(54) Title: CATALYST AND ITS USE IN THE SYNTHESIS OF HYDROGEN PEROXIDE

(57) Abstract: The present invention relates to a catalyst consisting of: (a) one or more metals of the platinum group as active components; (b) one or more polyolefins; and (c) a carrier. The invention also relates to a process for the synthesis of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) from hydrogen and oxygen which uses said catalyst and the use of the hydrogen peroxide solution in oxidation processes catalyzed by titanium silicalite. The process operates under high safety conditions with a high productivity and molar selectivity towards the formation of H<sub>2</sub>O<sub>2</sub>.

WO 03/014014 A3

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/EP 02/08546

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C01B15/029 C01B21/26 B01J23/42 B01J23/44 B01J31/06  
C07D301/12 C07C249/04 C07D303/04

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 C01B B01J C07D C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)  
EPO-Internal, WPI Data, PAJ, CHEM ABS Data, INSPEC, COMPENDEX

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 99 02264 A (MURCHISON CRAIG B ; HAYES DAVID A (US); WEBB STEVEN P (US); DOW CHE) 21 January 1999 (1999-01-21)	1,2,7, 12,18, 45-47, 50-52, 55, 58-60, 66,67
Y	page 2, line 35 -page 4, line 24 claims 1,8-10,12,14,18	4-6, 8-11, 13-15, 19-25, 48,49, 53,54, 56,57, 61-64

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents:

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \*G\* document member of the same patent family

Date of the actual completion of the international search

21 February 2003

Date of mailing of the international search report

28/03/2003

Name and mailing address of the ISA  
European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Rhodes, K

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/EP 02/08546

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6 210 651 B1 (HERRMANN WOLFGANG ET AL) 3 April 2001 (2001-04-03) column 1, line 67 -column 4, line 65 claims 1,12-15	1-3,7, 12,16
Y		4-6, 8-11, 13-15, 19-25, 48,49, 53,54, 56,57, 61-64
Y	WO 98 16463 A (BASF AG ;FLICK KLEMENS (DE); KAIBEL GERD (DE); STAMMER ACHIM (DE);) 23 April 1998 (1998-04-23)  claims 1,5-9,12-15 page 4, line 4-16 page 5, line 10-19 page 6, line 26-40 page 8, line 38 -page 9, line 31 examples	19-25, 48,49, 53,54, 56,57, 61-64
X	EP 0 100 119 A (ANIC SPA) 8 February 1984 (1984-02-08) cited in the application claims	68
X	US 3 714 342 A (KABISCH G) 30 January 1973 (1973-01-30) claims 1-6	69
P,A	EP 1 160 196 A (ENI SPA ;ENICHEM SPA (IT)) 5 December 2001 (2001-12-05) the whole document	1-69
A	US 4 832 938 A (GOSSER LAWRENCE W ET AL) 23 May 1989 (1989-05-23) claims 1-4 column 1, line 48 -column 2, line 2 examples	1-67
A	EP 0 366 419 A (ATOMIC ENERGY OF CANADA LTD) 2 May 1990 (1990-05-02) the whole document	1-67
A	EP 0 492 064 A (MITSUBISHI GAS CHEMICAL CO) 1 July 1992 (1992-07-01) column 3, line 3 -column 4, line 4 column 5, line 1-15 examples claims 1-7,10	1-67

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 02/08546

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 9902264	A	21-01-1999	AU 8067598 A WO 9902264 A1	08-02-1999 21-01-1999
US 6210651	B1	03-04-2001	AU 1994399 A AU 1994499 A CA 2315618 A1 CA 2315719 A1 CN 1283165 T CN 1283166 T EP 1042220 A1 EP 1042221 A1 JP 2001526167 T JP 2001526168 T WO 9932398 A1 WO 9932399 A1 US 6299852 B1	12-07-1999 12-07-1999 01-07-1999 01-07-1999 07-02-2001 07-02-2001 11-10-2000 11-10-2000 18-12-2001 18-12-2001 01-07-1999 01-07-1999 09-10-2001
WO 9816463	A	23-04-1998	DE 19642770 A1 AT 230705 T AU 725799 B2 AU 5119198 A BR 9711924 A DE 59709121 D1 WO 9816463 A1 EP 0946409 A1 JP 2001501904 T KR 2000049107 A US 2001003578 A1	23-04-1998 15-01-2003 19-10-2000 11-05-1998 25-04-2000 13-02-2003 23-04-1998 06-10-1999 13-02-2001 25-07-2000 14-06-2001
EP 0100119	A	08-02-1984	IT 1152299 B AT 21896 T CA 1196925 A1 DE 3365871 D1 DK 341483 A EP 0100119 A1 JP 1721832 C JP 4005028 B JP 59051273 A NO 832722 A ,B, US 4833260 A	31-12-1986 15-09-1986 19-11-1985 09-10-1986 29-01-1984 08-02-1984 24-12-1992 30-01-1992 24-03-1984 30-01-1984 23-05-1989
US 3714342	A	30-01-1973	DE 1945754 A1 AT 343078 B AT 823370 A BE 756015 A1 CA 934934 A1 CH 557781 A CS 157109 B2 ES 383264 A1 FR 2061634 A5 GB 1326282 A NL 7012327 A PL 81017 B1 SE 373111 B TR 17209 A YU 219470 A1 ZA 7006179 A	19-05-1971 10-05-1978 15-09-1977 15-02-1971 09-10-1973 15-01-1975 23-08-1974 01-01-1973 25-06-1971 08-08-1973 12-03-1971 30-08-1975 27-01-1975 02-05-1976 28-02-1982 28-04-1971

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 02/08546

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 1160196	A	05-12-2001	IT MI20001219 A1	03-12-2001
			EP 1160196 A1	05-12-2001
			JP 2002029711 A	29-01-2002
			US 2002028174 A1	07-03-2002
US 4832938	A	23-05-1989	AU 608976 B2	18-04-1991
			AU 3476089 A	16-11-1989
			BR 8902234 A	09-01-1990
			CA 1312720 A1	19-01-1993
			CN 1037874 A ,B	13-12-1989
			EP 0342048 A2	15-11-1989
			NZ 229087 A	28-08-1990
			PT 90542 A	30-11-1989
			TR 24229 A	03-07-1991
EP 0366419	A	02-05-1990	CA 1317740 A1	18-05-1993
			DE 68917255 D1	08-09-1994
			DE 68917255 T2	19-01-1995
			EP 0366419 A1	02-05-1990
			JP 2258610 A	19-10-1990
			US 5082647 A	21-01-1992
EP 0492064	A	01-07-1992	CA 2052009 A1	28-06-1992
			DE 69101775 D1	26-05-1994
			DE 69101775 T2	22-09-1994
			DE 492064 T1	05-11-1992
			EP 0492064 A1	01-07-1992
			JP 4357105 A	10-12-1992
			US 5132099 A	21-07-1992

**THIS PAGE BLANK (USPTO)**